

Extended Application of a Proven, Low Cost, Water Mitigation Treatment

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Final Technical Report

by

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Abstract:

The original Glass silicate system was evaluated in the lab for water shutoff field applications in oil and gas wells. In the effort to improve that system, a new silicate-polymer based, multi-component gel formulation, now called SPI Gel Technology, was discovered. It is felt that this is an important finding for industry which has been funded by the Stripper Well Consortium. The bulk of this project's time and funding was spent on evaluating this new gel formulation by laboratory testing to first define the matrix parameters that impact SPI gel formation (delayed gel timing and resultant gel properties) for water mitigation, casing repairs and other applications. A US patent application has been submitted for this new technology. All project tasks, except Task 6- Field Testing, have been accomplished. Task 6 was deferred to allow for further lab testing of the new SPI Gel system. We are now preparing to go into the field (with laboratory backup) for initial pressure testing of the SPI system in actual oil field wells. This project is being continued by SWC contract 3180-IT-USDOE-2098.

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Experimental Work: Experimental work was performed in Tasks 3, 4 and 5 in this project. Almost 500 laboratory tests were conducted during this project toward evaluating the original Glass process and the new SPI Gel Technology. The SPI test matrix included the following (generic) parameters in evaluating gel times and resulting gel properties: silicate concentration, polymer concentration, polymer types, other components concentrations & types, pH, temperature, mixing, brines/ cations/ multivalent ions, shearing, gel strength (final and over time), and other factors deemed important to the process. While the SPI gel process has been defined, it has not been fully evaluated and this lab work continues. Based on the laboratory findings to date the process is considered an important technology improvement for the industry due to its low cost materials, flexible gel times and gel properties and environmentally friendly components (i.e. no heavy metal crosslinkers). A patent application has been filed with the United States Patent Office on 28 November of 2006 covering this new formulation. While a patent application has not been published and, thus, the specific chemical formulation and lab work results must be held confidential (ie., proprietary) until publication. However, approved selections from the patent application are discussed in the Appendix C.

Executive Summary:

The original Glass silicate system was evaluated in the lab for water shutoff field applications in oil and gas wells. We talked to many silicate, polymer and water shutoff experts in the industry. We also performed a very complete SPE literature review and a very detailed patent search and review of existing silicate and polymer processes. In the effort to improve that Glass silicate system, a new silicate-polymer based (multi-component, single stage pumped) gel formulation, now called SPI Gel Technology, was discovered. It is felt that this is an important finding for industry, which has been funded by the Stripper Well Consortium. All project tasks, except Task 6- Field Testing, have been accomplished. Task 6 was deferred to allow for further lab testing of a newly discovered gel system. The bulk of this project's time and funding was spent on evaluating this new gel formulation by laboratory testing to first define the matrix parameters that impact SPI gel formation (delayed gel timing and resultant gel properties) for water mitigation, casing repairs and other applications. A US patent application has been submitted for this new technology. We are now preparing to go into the field (with laboratory backup) for initial pressure testing in actual oil field wells. This project is being continued by SWC contract 3180-IT-USDOE-2098 entitled "Novel Single Stage Water Mitigation Treatment".

In a sign to the importance of this technology, the Oklahoma Center for Advancement of Science and Technology (OCAST) approved additional funding for SPI gel development toward casing repair applications. These (SWC and OCAST) projects were joined to allow sharing of common development data so that lab tests would not have to be repeated and allowing both projects to progress further and faster than individually. After field proving, this technology will be made available to industry (via sale or license) for commercial applications in the very near future.

Introduction:

In many areas of the oil and gas industry, and especially for many stripper wells, operators handle 7 barrels of excess, unproductive water for every one barrel of crude oil (PTTC water conformance workshop, August 2004 in Houston, Texas). The University of Texas-Austin's Center for Petroleum & Geosystems Engineering (www.cpge.utexas.edu/pe/water_shutoff.html) reports that 20 billion barrels of water are re-injected in the US every year. Shell reported producing 6.29 million barrels of water in 2000, Elf-Aquitaine reported producing 1 barrel of water for every 1 barrel of oil, and Total reported producing 3 barrels of water for every barrel of oil it produces (per www.dordis.lu/data/PROJ_JOULE/ACTIONeqDndSESSIONeq5715200595ndDOC). This unwanted water increases the cost to produce every barrel of crude oil or mcf of natural gas due to the cost of lifting to surface, processing, treating and disposing/ re-injection of that excess and unwanted water. This cost to industry is estimated by the authors to be between \$2 billion (at \$0.10/bbl water) to \$5 billion (at \$0.50/bbl water). If that cost is translated into the price of crude oil, this water handling would cost between \$0.70 to \$3.50 per barrel of every produced crude oil. Such excess water also reduces oil and gas reserves due to the increased operating cost (uneconomic earlier) and due to the damaged reservoir's rock flow properties (relative permeability and imbibition) concerns.

Some oilfield processes utilize injected water (waterfloods) to move oil from the reservoir rock into the wellbore where it can be lifted to the surface and sold. Other processes utilize injected water to maintain reservoir pressure to allow additional oil to be recovered than if the pressure were allowed to drop. However in both processes, the efficient use of the injected water is desired. Cycling of the water between the injection well and production well and back into the injection well causes increased repeated handling costs.

Other oilfields have unwanted water production native to the reservoir and not due to injection of any water. This is due to the naturally occurring fluids in the original reservoirs (examples are Arbuckle and Hunton formations) allowing both to flow to the well. Even in these 'primary' production operations, when water production gets too high for the amount of oil or gas produced, the operation becomes uneconomic, production is stopped and the well is plugged.

Drilling also has problems with unwanted water production. Air drilling is often stopped because water influx cannot be lifted to the surface with

available volume/pressure air compressors. Thus efficient air drilling must be converted to less efficient mud drilling at that point. Plugging off that water influx would allow efficient air drilling to continue deeper.

Drilling operations may also be stopped due to loss of circulating mud into high permeability zones, just the opposite of unwanted water production. However the remedy of plugging off this high permeability zone to solve this problem is similar to excess water, allowing drilling to continue.

Excess water production also comes from holes in the casing from wear, erosion, corrosion (inside and outside) and tectonic forces. Repair of that rupture would stop that unwanted water production. For injection wells, such holes or ruptures can cause the well to be taken out of service and plugged.

Many methods have been employed by industry to reduce this excess water over the last century including: mechanical means (wellbore equipment to isolate the influx depth interval); cement across and into the offending zone; chemical means including silicates, polymers, cross linked polymers, grouts, and epoxies; and specifically placed horizontal laterals. It is interesting to note that silicates were utilized before crosslinked polymers in the oilfield's attempts to reduce water production.

Mechanical equipment and cements are mostly limited to the wellbore and thus are important but not the best method for all occasions. Epoxies are very expensive and normally reserved for casing repairs and small volumes. Indepth methods to permanently or not permanently reduce or redirect water are primarily polymers and crosslinked polymers. The polymers utilized are mostly polyacrylamides. Crosslinking of the polymer is normally accomplished with heavy metal chrome and an activator. Many and most governmental agencies are moving away from such heavy metals due to environmental concerns. This is especially true when treatments are in fresh or 'treatable' water zones. Field treatments of these systems are only about 60% to 90% successful depending on operator experience (2004 PTTC workshop). Other reports suggests that such near-wellbore treatments are less than 45% successful (www.dordis.lu/data/PROJ_JOULE/ACTIONeqDndSESSIONeq5715200595ndDOC).

A more effective and lower cost method to reduce or stop this unwanted water production is needed by industry. Silicates hold the promise of a lower cost and more environmentally friendly alternative than current

chrome crosslinked polymer or epoxy systems. However most silicate systems are difficult to use, difficult to control and can form brittle precipitates. Properly utilizing silicates and finding an improvement to that system was the promise of this project.

Project Tasks

This Project's original and primary goal was to improve and field test an existing low cost two-stage silicate water mitigation treatment, known as the Glass system. To do this we were tasked to –

1. Perform a more complete literature search and review of the existing silicate processes in the industry;
2. Talk to leading experts in the industry and academia;
3. Better understand the Glass silicate system chemistry for more accurate/ successful treatments can be performed;
4. Investigate methods to use brines for mix and buffer waters for cost savings;
5. Investigate methods to allow a single stage pumped silicate systems for better performance and easier field handling; and
6. Perform field treatments.

All but Task 6 has been accomplished, as will be discussed in later sections. From Task 5 a new gel system was discovered and a US patent applied.

Project Milestones:

- February 2005 SWC proposal submitted
- April 2005 SWC meeting to present proposal
- 25 April 2005 Notification of project acceptance by SWC at a reduced funding level of \$107,200 and 70% cost share
- June 2005 Notification of SWC award on project
- 22 Sept 2005 SWC contract awarded for project
- Fall 2005 SWC meeting in San Antonio TX, presentation on project status and discussion with Paul Willhite
- Fall 2005 Teleconferences w/ Randy Seright, Robert Sydansk and other experts in the field
- Fall 2005 Researched laboratories with silicate experience
- January 2006 Hired TEPCO/ RTA lab headed by Lyle Burns
- 20 Jan 2006 Contract and IP agreement with all project parties
- Feb 2006 First full project group meeting in Bartlesville OK
- 6 Feb 2006 Report on research of literature on related systems
- 13 Feb 2006 Report on research of patents on related systems
- Feb 2006 Discovered and confirmed new SPI formulation
- 20 Feb 2006 Teleconference with Robert Sydansk
- 27 Feb 2006 Teleconference with Betty Felber
- 27 Feb 2006 Teleconference with Sam Sarem
- 31 March 2006 Technical Progress Report
- 4 April 2006 SWC meeting in University Park, PA
- April 2006 Prepared matrix of all known parameters that influences SPI formulation gel times and gel strengths/ properties
- Summer 2006 Tested various chemical systems, salts, pH, polymer type, extrusion test, temperature, additives,
- Summer 2006 Tested SPI formulation boundaries to determine range and properties of gels
- Summer 2006 Second patent search and review- over 100 patents
- 30 June 2006 Technical Progress Report
- 1 July 2006 Awarded contract from the Oklahoma Center for the Advancement of Science and Technology (OCAST) for a related project on using the SPI gel for casing repairs.
- Summer 2006 Continued process development in the lab on understanding the full SPI system.
- 31 September 06 Technical Progress Report
- July-Oct 2006 Obtained field oil and waters for laboratory testing

- 18 August 2006 Filed a DOE Report of Invention Disclosure form on the new SPI Gel Technology
- 29 August 2006 Received SWC approval to modify budget and tasks, primarily to officially defer Task 6 into second SWC project.
- Sept 2006 Designed/prepared extrusion apparatus (not finished)
- Sept 2006 Designed/prepared coreflood apparatus (not finished)
- 26 Oct 2006 Booth at the Oklahoma Marginal Well Commission's Oklahoma City Trade Fair
- 9 Nov 2006 SWC Meeting presentation in Pittsburgh, PA
- 28 Nov 2006 Filed SPI Gel Technology patent at US Patent Office with reservation for foreign filings
- 31 Dec 2006 Final Technical Report- draft for approvals
- 15 Jan 2006 Submitted Final Report to Stripper Well Consortium

Discussion

After discussions with selected experts in the water mitigation field (Paul Willhite, Randy Seright, Betty Felber and Bob Sydansk), review of Union Oil Company of California's (UNOCAL) earlier silicate work and a review of silicate laboratories and silicate experts, we hired RTA Systems for our silicate chemistry advisor and testing laboratory. RTA Systems, Lyle Burns and Jim Hessert have extensive knowledge of silicates and PAMs uses in industry. Upon agreement of intellectual property rights, we began reviewing current and targeted changes in the Glass silicate system.

After performing a very complete literature (Appendices A and B) and patent search (portions of Appendices B and C) and reviewed existing silicate and polymer water shutoff/ mitigation processes, we better understood the existing Glass silicate system, satisfying Task 1 and 3. RTA then performed gel tests on selected silicate (multi-component) mixes for improving the Glass silicate system, Task 5. A specific multi-component silicate-polymer mixture was found that provides many of the attributes desired in a single stage, controlled delayed gel system, which we now call the SPI Gel Technology. Multivalent ions were tested against the SPI gel with up to 3% KCl tested, Task 4.

Next, we talked to several industry experts/ consultants, including Bob Sydansk, Sam Sarem, and Betty Felber to fulfill Task 2 and better understand the full range of systems available in the industry. Dr. Felber was very intelligent and helpful in understanding silicate, lignosulfonates and PAM chemistry and their applications. Mr. Sydansk provided a very concise review of polymer systems. Methods of chelating or precipitating the problematic multi-valent ions were identified and confirmed by Dr. Sarem.

Additional lab tests of the SPI gels have been continued to outline the range of applicability and find 'show-stoppers', however no such process "stoppers" have been found. With permission from SWC, we put further lab work and all field testing on the original Glass silicate treatment method on permanent hold and deferred field testing of the new SPI system until laboratory work was sufficient to go to the field. A new and expanded (over 100 patents) patent search and review was performed concerning the new formulation with no similar technology was uncovered, Task 1 renewed. A patent was filed on 28 November 2006 for this new, SWC supported technology development.

The SPI Gel Technology is basically a multi-component silicate system, where one of the components includes a polymer. It uses no heavy metal crosslinkers which makes it much more environmentally friendly than most all current gel systems. The various combinations of components makes the system very versatile in controllable delayed gel times (from immediate to days) and gel strengths (thickening to hard ringing gels). The rest of the composition is proprietary and will not be disclosed until published by the US Patent Office. Examples of the formed gels have been shown at various SWC meetings, with a picture of such a formed gel shown below.



Figure 1- SPI gel example

The formulation has many potential uses, as identified in the patent, such as oil and gas well casing repairs, oil and gas reservoir profile (vertical and areal) flow modification, surface pipe repairs (utility conduits, buried ductwork, sewer lines, etc...), grouting and other uses.

Further laboratory testing is continuing and all field testing work is under a second SWC project, contract #3180-IT-USDOE-2098 entitled “Novel Single Stage Water Mitigation Treatment”. Field mixing and injection equipment are being assembled at the time of this report writing.

Conclusions:

Using Stripper Well Consortium (via Penn State University and US Department of Energy) grant funding, we have discovered a new single stage, multi-component, controlled delayed gelation silicate based gel system for water mitigation and casing repair for the nation's stripper well operators and over 400,000 stripper wells. The new gel system, called the SPI Gel Technology, is made from low cost materials and is much more environmentally friendly than existing chrome based gel polymer systems. It allows a wide range of mixture combinations yielding a wide range of gel outcomes- from ringing hard to softer to 'lipping' gels to hard brittle gels. It also has applications in utility line repairs, oil and gas drilling, construction grouting and many other applications. This project is being continued by SWC contract 3180-IT-USDOE-2098 entitled "Novel Single Stage Water Mitigation Treatment" for further defining the SPI gel's control methodology and performance matrix parameters, provide lab support for field testing and perform numerous field tests. The subsequent (to field proving) sale of technology or licensing will get this technology rapidly into commercial usage.

References: See Appendices A (summary of key SPE papers), B (list of relevant SPE papers), C (patents discussion) and D (list of key patents and papers).

Bibliography: None

Appendices:

- A - Summary discussion of key SPE papers
- B - Listing of relevant SPE papers
- C - Discussion of relevant patents
- D - Listing of key patents and additional technical papers

APPENDIX A

Summary of Key SPE Papers on Silicate and Related Gel Systems

Reviewed 8Feb06

SPE 09104

"Preliminary Laboratory Tests And The Interpretation Of The Results With Reference To The Mechanism Of Residual Oil Mobilization",

Z.Heinemann, G.Milley, O.Wagner

Laboratory discussion of successive injection of sodium metasilicate and calcium chloride solutions into the porous medium so that a gel precipitation will take place in-situ. A succession of two series was found to be the optimum Process included a silicate solution containing 2 w% SiO₂ and then with 7 w%, both followed by the calcium chloride solution to provide a divalent cation for the reaction with sodium orthosilicate. Gives good silicate solution characteristics and properties.

Good earlier references from that paper-

AM Sarem, "Secondary and tertiary recovery of oil by MCCF process", SPE Reprint 4901, (1974).

JR Johnson, "Status of Caustic and Emulsion Methods", J.Pet.Tech. , 1/76, 85-92 (1976)

DT Masan, MC Shah, K Sampath, R Shah, "Spontaneous Emulsification and the Effect of Interfacial Fluid Properties on Coalescence and Emulsion Stability in Caustic Flooding".

SPE 12473

"Selective Gas Shut-Off Using Sodium Silicate in the Prudhoe Bay Field, AK",

G.D. Herring, J.T. Milloway, W.N. Wilson

Discussed diluted (16% 40 Baume' sodium silicate and 84% water) and concentrated (40 Baume') sodium silicate Corefloods of dilute and concentrated silicate systems were evaluated. Two different activating agents (not identified) designed to gel the sodium silicate were reviewed. Halliburton activators Salt pellets and polymer were used as diverting agent for oil zones. In field tests, operator had to wash out and reperforate the wells, but it was successful

SPE 13578

"Profile Modification and Water Control With Silica Gel-Based Systems",

P.H. Krumrine* and S.D. Boyce

1985

Very good review of silicate systems and related patents, lignosulfonates, CO₂ and other systems. This paper presents the chemistry of silica polymer gel systems and review of their properties, benefits, limitations and methods of application. The properties such as gel time, strength and shrinkage vary considerably versus the concentrations of reactants, the particular reservoir environmental conditions such as temperature, salinity, hardness, and hydrocarbon maturation. Gels ranging from elastic to rigid can be made with set times area. By achieving either partial or total varying from a few seconds to several hours Inorganic acids and reactants such as CaCl or NaAlO₂ tend to react quite rapidly Organic reactants that slowly hydrolyze or oxidize give more gradual formation of gels. Host reservoirs that contain high salinity, hardness, or temperature environments tend to accelerate the gel formation

SPE 17674

“Reservoir Water Control Treatments Using a Non-Polymer Gelling System” ,
KS Chan- Dowell

2-5 February 1985

This paper discusses a non-polymer, binary system using an organic salt solution with an activator that increases pH as it slowly dissolves, the salt then gels. Claimed that it is very tolerant of salinity, i.e. salts. It is pumped as one system. The system uses only two chemicals- The first one is an inorganic salt which can be dissolved in any mix water up to 60% w/v. The solution has a pH of 4 to 4.4. The second chemical is a low molecular weight organic compound which decomposes with time and increases the pH of the solution. At pH 5.5, the fluid starts to thicken and forms a gel which has been identified to be a network of fine colloidal particles. The strength of the gel increases with increasing pH until the pH reaches about 7. The average particle size varies depending on the salinity and the hardness of mix water- generally of the order of 0.1 micron.

SPE 17949

“Design and Field Application of Chemical Gels for Water Control in Oil Wells Producing From Naturally Fractured Carbonated Reservoirs”,

NN. Senol, R GiNumser, N. Tekayak

1989

Lab and field work was done and reported on silica gel system and a polymer system in Turkey. No specifics given on the activators mentioned for silicates.

SPE 18505

“Oilfield Applications of Colloidal Silica Gel”,

J.J. Jurhrak, SPE, and L.E. Summers
1989

After a wide range of gel chemistries were screened, the search focused on silica-based systems. Colloidal silica gels were selected for development instead of conventional sodium silicate gels because of their more robust gel-time control. Following extensive laboratory testing, field testing of colloidal silicates, as differentiated from sodium silicate, were used. Casing repair, prod and injection well field treatments were reported. Silica solution was neutralized with HCl on the surface before pumping. Report from lab tests that sodium silicate viscosity is about same as water, but injectivity is $\frac{1}{2}$ of water in most formations and, in clay formations, up to $\frac{1}{10}$ of water. Colloidal system require fresh water in mixing.

SPE 19896

“Enhanced Alkaline Flooding”,
Harry Surkalo
Alkaline flooding only

SPE 20997

“Reversible In-Situ Gelation by the Change”,
S. Vossoughi, A Putz
Kansas State new polymer- pH activated with acid.

SPE 37466

“A Successful Water Shut off – A Case Study from the Stratfjord Field”,
Raymond Boreng and Ove Birger Scendsen
Silicate treatment (no detail given) of one well...very successful

SPE 39617

“Water Shutoff Treatments in Eastern Alberta: Doubling Oil Production,
Decreasing Water Cut “,
E. Samari, D.L.T. Scott, D. Dalrymple,
1998

Discussion of delayed gel silicate system with ultrafine cement. Ethyl acetate was used (Halliburton). Gel control was accomplished by lowering pH before pumping. Reacts with divalent ions (cation or anions?) to form a gel.

SPE 49464

“Case Histories of Successful Water Shutoff Techniques Utilized in Enhancing Oil Output from Minagish Oolite Reservoir of East Umm Gudair (West Kuwait)”

ML Chawla, A Al-Otaibi and A Waheed
1998
Halliburton InjectrolG treatments reported

SPE 49468

“Field Advanced Water Control techniques using Gel Systems”,
P Baylocq, JJ Fery and A Grenon
1998

Several field applications of different gel systems including sodium silicates. 4 drilling applications of colloidal suspended sodium silicate which were externally activated with a 10% CaCl₂ reactive brine.

SPE 50760

“High-Density Monomer System for Formation Consolidation/Water Shutoff Applications”,
L Eoff, GP Funkhouser, M Cowan
1999

Hydrogenperoxide and azo initiators were used for polymerizing solutions of 2-hydroxyethyl acrylate in aqueous solutions of sea salt, sodium chloride (NaCl), calcium chloride (CaCl₂), calcium bromide (CaBr₂), and zinc bromide (ZnBr₂) with densities from 8.6 to 17.5 lbm/gal. These have been formulated for heavy brines or cool temperatures.

SPE 53312

“Conformance-While-Drilling Technology Proposed to Optimize Drilling and Production”
R Sweatman, J Heathman, R Faul, N Gazi,
1999

Lists many plugging/gel systems possible on page 4

SPE 56739

“Application of Silicate-Based Well Treatment Techniques at the Hungarian Oil Fields”
I Lakatos, EJ Lakatos-Szabó, G Tiszai, G Palásthy, B Kosztin, S. Trömböczky
M Bodola, G Patterman-Farkas
1999

Excellent paper on review of silicate and combination systems. Hungarian work identified joint application of silicates and polymers or humates, in a multifunctional, self-controlling chemical system is usually formed which works

spontaneously even under harsh reservoir conditions, meanwhile the methods remain inexpensive, flexible and adaptable to any production technology. A concise summary of the diverse techniques, their principle and mainly field projects are discussed in the paper. It was shown that the silicates, combined with polymers and humates offer unique opportunity to cure numerous production/injection problems including water-shut-off, profile correction, clay stabilization, etc. in oil and gas fields and underground gas storage. Between 1980 and 1998 the field projects, comprising more than hundred well treatments, yielded substantial additional oil production, life time of wells. Excellent paper

SPE 59322

“Evaluation of Gelation Systems for Conformance Control”

A Prada, F Civan, ED Dalrymple

Halliburton Energy Services, Inc.

2000

Halliburton Energy Service paper which talks about and compares 4 gel systems, but does not say what they are! Of no use.

SPE 60896

“Use of Temperature Simulations in Water-Control Design”

MA Hardy, DW van Batenburg, CW Botermans,

Discusses temperature estimation methods which can control gel times

SPE 69675

“Silica Micro-Encapsulation Technology for Treatment of Oil and/or Hydrocarbon-Contaminated Drill Cuttings”

L Quintero, JM Limia, S Stocks-Fischer

Nothing specific for reservoir water control.

SPE 70067 & 84966

“A Strategy for Attacking Excess Water Production”

R. S. Seright, R H Lane, R D Sydansk

Discusses how to identify and solve specific water production problems. Good references

SPE 72119

“Chemical Water & Gas Shutoff Technology - An Overview “,

AH Kabir

Excellent paper on all types of sealants including many silicates. Excellent overview.

SPE 77414

“Relative Permeability Modification Using an Oil-Soluble Gelant to Control Water Production”

GP Karmakar, CA Grattoni, RW Zimmerman

2002

Discuss silicate methods for delayed gelation. Focus on a new oil soluble silicate system (Tetramethylorthosilicate or TMOS) which is mixed with oil and injected into the formation and allows for preferential permeability change. When it comes into contact with water it hydrolyses and gels.

SPE 78351

“Field Evaluation of Iron Hydroxide Gel Treatments”,

B Kosztin, G Palasthy, F Udvari, L Benedek, I Lakatos

2002

Hungarian development of a old method. Found not as effective as polymer /silicate treatments, but still 60% technically successful and 40% profitable.

SPE 80206

“Development of a Hydrophobically Modified Water-Soluble Polymer as a Selective Bullhead System for Water-Production Problems”,

L Eoff, S Dalrymple, BR Reddy, J Morgan, H Frampton

Discussed a polymer not silicate system, but interesting bullhead system that protects oil bearing zones.

SPE 84904 & 89452

“Selected US Department of Energy’s EOR Technology Applications”,

B Felber

2003

Good overview of ASP, CO2 viscosifiers, microhole drilling and tools...however, nothing on silicates

SPE 92339

“High-Temperature Plug Formation with Silicates”,

S Bauer, P Gronewald, J Hamilton, D LaPlant, A Mansure

High temperature silicate plug

SPE 75163

“A Natural Polymer-Based Crosslinker System for Conformance Gel Systems”,
BR Reddy, L Eoff, ED Dalrymple, K Black, D Brown, M Rietjens
2002

A good review of the benefits and problems associated with many crosslinkers for polymer systems, many of which are being phased out by various governmental agencies. The paper presents laboratory work on a crosslinker for acrylamide polymers based on naturally occurring chitosan.

APPENDIX B

Listing of Key SPE papers

12473-MS **Selective Gas Shut-Off Using Sodium Silicate in the Prudhoe Bay Field, AK**

70067-MS **A Strategy for Attacking Excess Water Production**

37466-MS **A SUCCESSFUL WATER SHUT OFF. A CASE STUDY FROM THE STATFJORD FIELD**

56739-MS **Application of Silicate-Based Well Treatment Techniques at the Hungarian Oil Fields**

66565-PA **Scale Dissolver Application: Production Enhancement and Formation-Damage Potential**

19896-PA **Enhanced Alkaline Flooding**

80206-MS **Development of a Hydrophobically Modified Water-Soluble Polymer as a Selective Bullhead System for Water-Production Problems**

72119-MS **Chemical Water & Gas Shutoff Technology - An Overview**

96945-MS **Relative Permeability Modifier Treatments on Gulf of Mexico Frac-packed and Gravel-packed Oil and Gas Wells**

9104-MS **GEL DISPLACEMENT - AN ENCOURAGING NEW METHOD FOR INCREASING ULTIMATE OIL RECOVERY**

11970-MS **Porosity Reduction in Sandstone**

60896-PA **Use of Temperature Simulations in Water-Control Design**

59322-MS **Evaluation of Gelation Systems for Conformance Control**

66558-PA **More Than 12 Years' Experience With a Successful Conformance-Control Polymer-Gel Technology**

13578-MS **Profile Modification and Water Control With Silica Gel-Based Systems**

78351-MS **Field Evaluation of Iron Hydroxide Gel Treatments**

53312-MS **Conformance-While-Drilling Technology Proposed to Optimize Drilling and Production**

20997-MS **REVERSIBLE IN-SITU GELATION BY THE CHANGE OF PH WITHIN THE ROCK**

84966-PA **A Strategy for Attacking Excess Water Production**

17811-MS **How To Solve Lost Circulation Problems**

49468-MS **Field Advanced Water Control Techniques Using Gel Systems**

18505-PA **Oilfield Applications of Colloidal Silica Gel**

92339-MS **High-Temperature Plug Formation With Silicates**

69675-PA **Silica Micro-Encapsulation Technology for Treatment of Oil and/or Hydrocarbon-Contaminated Drill Cuttings**

49464-MS **Case Histories Of Successful Water Shutoff Techniques Utilised In Enhancing Oil Output From Minagish Oolite Reservoir Of East Umm Gudair, (West Kuwait).**

17674-MS **Reservoir Water Control Treatments Using a Non-Polymer Gelling System**

89452-MS **Selected U. S. Department of Energy EOR Technology Applications**

17949-MS **Design and Field Application of Chemical Gels for Water Control in Oil Wells Producing From Naturally Fractured Carbonated Reservoirs**

84904-MS **Selected U.S. Department of Energy's EOR Technology Applications**

Subtotal

Estimated sales tax: (Texas addresses only)

Total

APPENDIX C
Summary of Key Patents and Technical Papers
(Taken from SPI Gel Technology US patent application-28 November 2006)

The mobility of any fluid in a permeable geological formation is the effective permeability of the formation to that liquid divided by the viscosity of the fluid. Thus, a commonly developed method for reducing the mobility of a particular fluid in a permeable geological formation is to increase its viscosity such as by using viscous solutions of partially hydrolyzed polyacrylamides such as described by Sandiford et al in US 2,827,964 and McKennon US 3,039,529

Application of silicates in different industrial areas is well documented. Injection of silicate solutions into reservoirs with the aim at enhancing the recovery factor through a diverting effect was proposed by Ronald Van Auken Mills in US 1,421,706 in 1922. Acidic gel systems may be the oldest and most commonly employed techniques that employ silicates. These gels are more accurately described as precipitation type gels since they are extremely brittle with virtually no elasticity. In the early 1960's, sodium silicate and glyoxal were combined (US 3,028,340) to make various hard cement-like coatings on substrates. At low concentrations a firm gel was obtained that lacked cohesiveness and was not as hard as cement. In 1964, Gandon et.al. (US 3,149,985) took went a step further and cited sodium silicate reactions with other "reactive carbonyl" compounds such as polyalcohol esters to make cement like substances. One goal of these technologies was to make agents to generate very hard consolidated soils for constructing structures such as bridges, dams and water reservoirs on the soil surface. Throughout the last 50 years numerous inventors patented various sodium silicate systems (US 2,747,670, US 2,807,324, US 3,435,899, US 4,461,644, US 4,640,361, US 6,059,035 and US 6,059,035 all of which patents are incorporated herein by reference) to make gels for use in plugging high permeability areas of oil and gas producing reservoirs.

In the literature, an SPE Paper #13578 presented by Krumrine and Boyce ("Profile Modification and Water Control With Silica Gel-Based Systems", P.H. Krumrine and S.D. Boyce, 1985) is considered a milestone because this paper is not only a complete summary of the topic listing numerous papers and patents on sodium silicate chemistry as applied to oil field and grouting applications, but they also drew attention to a controversial fact that the silicate use was inequitably neglected in commercial applications in favor of polymer treatments in practice at the time.

Although the sodium silicate technology was the first plugging and permeability modification technology largely put to practice, the use of gelled polymers based on polyacrylamide and chromium salts with reducing agents or organochromium compounds became more popular in the 1970's and 1980's because of their unique versatility to make hard and soft elastic gels rather than the inelastic gels formed using sodium silicate chemistry. Phillips Petroleum Company was a pioneer in this area and was later followed by Marathon Oil Company with similar technology using polyacrylamide-chromium gelled systems. For example, Needham in 1968, US 3,412,793, proposed the injection of

a stable foam into a high permeability formation. Other prior art proposed various gelled polymers, such as carboxyethyl and carboxymethyl cellulose (US 3,727,687, Clampitt et al, 1973), polyacrylamides and polymethacrylamides (US 3,749,172, Hessert et al, 1973), and various combinations and modifications of these (US 3,762,476, Gall, and US 3,785,437, Clampitt et al, 1974). At Marathon Oil Company, Argabright et al proposed the use of low molecular weight aldehydes as a crosslinking agent for polyacrylamide (US 4,098,337) in 1978 and later in 1984 Falk (US 4,485,875) proposed the use of phenol with formaldehyde as a crosslinking combination for polyacrylamides.

At Union Oil Company, Sandiford proposed improved methods (US 3,741,307 in 1973, US 4,004,639 in 1977, US 4,009,755 in 1977, and US 4,069,869 in 1978) to waterflooding whereby various combinations of polymer flooding with polyacrylamide and plugging of high permeability areas with sodium silicate and derivatives. In this method, following injection of enough polymer to penetrate between 20 – 50 feet from the wellbore, sequential slugs of chromates and the silicate technologies of the prior art are contemplated as a follow-in plug that substantially reduces the permeability of the more permeable strata of the formation to the subsequently injected flooding media. These systems constitute complex solutions containing chromium cross-linkers, reducing agents, silicates and silicate gelling agents known in the art.

Various methods are known in the art for preparing copolymers, e.g., (U.S. Pat. Nos. 2,625,529; 2,740,522; 2,729,557; 2,831,841; and 2,909,508). Such copolymers can be used in the hydrolyzed form, as discussed above for the homopolymers. Polyacrylic acids, including polymethacrylic acid, prepared by methods known in the art can also be used in the practice of the methods and composition of the present disclosure. Polyacrylates, e.g., as described in Kirk-Othmer, "Encyclopedia of Chemical Technology," Vol. 1, second edition, pages 305 et seq., Interscience Publishers, Inc., New York (1963), can also be used. Examples of such polyacrylates include polymers of methylacrylate, ethylacrylate, n-propylacrylate, isopropylacrylate, n-butylacrylate, isobutylacrylate, tert-butylacrylate, n-octylacrylate, and the like. Polyacrylate acrylamide copolymers may also be used.

Polymers of acrylamide and AMPS and/or vinyl pyrrolidone have better thermal and brine tolerance in oil field applications (Stahl et. al. US 5,382,371). These polymers have become known as the Hostile Environment (HE) polymers. HE polymers are highly tolerant to hydrolysis eliminating the formation of precipitates with divalent ions such as calcium and magnesium at high temperatures up to and including 300 F.

APPENDIX D

Full Patent List & Additional SPE Papers

- US 1,421,706
July 4, 1922, Ronald Van Auken Mills, Assignment: Self
“Process of Excluding Water From Oil & Gas Wells”
- US 2,402,588
June 25, 1946, Kurt H. Andresen , Assign to Essex Royalty Corp.
“Method of Oil Recovery”
- US 2,492,790
December 27, 1949, Ladislaw Vilmos Farkas et. al.
“Acid Resisting Cement and Method of Making”
- US 2,713,906
July 26, 1955, Josoph C. Allen, Assignment: The Texas Company
“Preventing Of Gas Coning In The Production of Oil From Combination Reservoirs”
- US 2,747,670
May 29, 1956, Jack A. King et. al., Assignment Cities Service
“Method of Increasing Oil Recovery”
- US 2,766,130
October 9, 1956, Karl Dietz et.al. Assignment: Hoechst
“Self-hardenting Water-glass Compositions and Process of Preparing Same”
- US 2,787,325
April 2, 1957, Orrin C. Holbrook, Assignment: Pure Oil Co.
“Selective Treatment of Geological Formations”
- US 2,799,341
July 16, 1957, George P. Maly, Assignment: Union Oil Co.
“Selective Plugging in Oil Wells”
- US 2,801,699
August 6, 1957, Assignment: Pure Oil Co.
“Process For Temporarily and Selectively Sealing A Well”
- US 2,807,324
September 24, 1957, Jack A. King et. al., Assignment: Cities Service Co.
“Method of Increasing Oil Recovery”
- US 2,837,165
June 3, 1958, Alan P. Roberts, Assignment: Esso Research & Engineering Co.
“Permanent Well Completion Apparatus”
- US 2,864,448
December 16, 1958, Donald C. Bond et. al. Assignment: Pure Oil Co.
“Process for Selectively and Temporarily Sealing A Geological Formation Having Zones of Varying Permeability”
- US 2,911,048
November 3, 1959, James R. DublinIII, Assignment: Jersey Production Research Co.
“Apparatus for Working Over and Servicing Wells”
- US 2,968,572
January 17, 1961, Cletus E. Peeler, Jr., Assig: Diamond Alkali Company

“Chemical Composition and Process For Soil Stabilization”
US 3,013,607
December 19, 1961, Donald C. Bond et. al. Assignment: Pure Oil Co.
“Selective Plugging Between Contiguous Strata”
US 3,028,340
April 3, 1962, Louis Gandon et al. Assignment: Societe Nobel Bozel
“Production of New Compositions From Glyoxal and Alkali Metal Silicates”
US 3,028,912
April 10, 1962, Virgil J. Berry, Jr. et.al., Assignment: Pan American Petroleum Corp.
“Recovery of Oil From an Underground Formation”
US 3,094,846
June 25, 1963, C. E. Peeler, Jr., Assignment:
“Treatment of Earth Strata Containing Acid Forming Chemicals”
US 3,141,503
July 21, 1964, Nathan Stein, Assignment: Socony Mobil Oil Co.
“Plugging of Permeable Earth Formations”
US 3,145,773
August 25, 1964, Robert M. Jorda et. al. Assignment: Shell Oil Co.
“Method of Sealing Formations in Completed Wells”
US 3,149,985
September 22, 1964, Louis Gandon et al. Assign: Petit-Quevilly, A French Company
“Preparation of Silica Gels From Alkaline Silicates and Polyalcohol Esters”
US 3,202,214
Aug. 24, 1965, Homer C. McLaughlin, Jr., Assignment: Halliburton
“Preparation and Use of Sodium Silicate Gels”
US 3,251,414
May 17, 1966, Bertram T. Willman, Assignment: Esso Production Research Co.
“Method For Control of Water Injection Profiles”
US 3,261,400
July 19, 1966, Elliot B. Elfrink, Assignment: Mobil Oil Corp.
“Selective Plugging Method”
US 3,288,040
November 29, 1966, Raymond C. Burrows Assignment: Archer-Daniels-Midland Co.
“Soil Stabilization”
US 3,294,563
Dec 27, 1966, David Rowland Assign: The Cementation Company Ltd.
“Silicate Grout”
US 3,308,884
March 14, 1967, Thomas J. Robichaux, Assignment: Shell Oil Co.
“Plugging Underground Formations”
US 3,342,262
September 19, 1967, Jack A. King et. al., Assignment: Cities Service Oil Company
“Method of Increasing Oil Recovery”
US 3,435,899
April 1, 1969, Homer C. McLaughlin et al, Assign: Halliburton
“Delayed Gelling of Sodium Silicate and Use Therefore”

US 3,439,744
April 22, 1969, Bryant W. Bradley, Assignment: Shell Oil Co.
“Selective Formation Plugging”

US 3,489,222
January 13, 1970, Ralph S. Millbone et. al., Assignment Chevron Research Co.
“Method of Consolidating Earth Formations Without Removing Tubing From Well”

US 3,522,844
August 4, 1970, Milton K. Abdo, Assignment: Mobil Corp.
“Oil Recovery Process With Selective Precipitation of Positive Non-Simple Liquid”

US 3,637,019
January 25, 1972, Jimmy D. Lee, Assignment: Dalton E. Bloom
“Method for Plugging a Porous Stratum Penetrated By A Wellbore”

US 3,656,550
April 18, 1972, Ovner R. Wagner Jr., Assingment: Amoco Production Co.
“Forming a Barrier Between Zones in Waterflooding”

US 3,695,356
October 3, 1972, Perry A Argabright, Assignment: Marathon Oil Company.
“Plugging Off Sources of Water In Oil Reservoirs”

US 3,700,031
October 24, 1972, Walter F. Germer, Jr. et. al. Assignment: Germer-Stringer Corp.
“Secondary Recovery and Well Stimulation, Solutions, and Methods of Use”

US 3,701,384
October 31, 1972, Willis G. Roatson, Assignment: Dow Chemical Co.
“Method and Compositions for Controlling Flow Through Subterreanean Formations”

US 3,727,691
April 17, 1973, Thomas W. Mucke et. al. Assignment: Esso Production Co.
“Method and Apparatus for Treating Subterranean Formations”

US 3,749,172
July 31, 1973, James E. Hessert & R. L. Clampitt, Assignment: Phillips Petroleum Co.
“Method of Using Gelled Polymers in The Treatment of Wells”

US 3,759,326
September 18, 1973, Charles A. Christopher Assign: Texaco, Inc.
“Secondary Oil Recovery Method”

US 3,762,476
October 2, 1973, James W. Gall, Assignment: Phillips Petroleum Company.

US 3,785,437
January 15, 1974, R.L. Clampitt & James E. Hessert, Assignment: Phillips Petroleum Co.
“Method For Controlling Formation Permeability”

US 3,804,173
April 16, 1974, Robert R. Jennings, Assignment: Dow Chemical Co.
“Method For Reducing Polymer Adsorption in Secondary Oil Recovery Operations”

US 3,876,002
April 8, 1975, Amir M. Sarem, Assignment: Union Oil Co.
“WaterFlooding Process”

US 3,897,827
August 5, 1975, Betty J. Felber et.al. Assignor: Standard Oil Co.

“Lignosulfonate Gels For Sweep Improvement In Flooding Operations”
US 3,920,074
November 18, 1975, Amir M. Sarem, Assignment: Union Oil Company
“Method For Improving The Injectivity Of Water Injection Wells”
US 3,955,998
May 11, 1976, R.L. Clampitt and James E. Hessert, Assignment: Phillips Petroleum Co.
“Aqueous Gels For Plugging Fractures In Subterranean Formation and Production OF
Said Aqueous Gels”
US 3,965,986
June, 29, 1976, Charles A. Christopher, Assign: Texaco, Inc.
“Method For Oil Recovery Improvement”
US 3,993,133
November 23, 1976, Richard L. Clampitt, Assignment: Phillips Petroleum Co.
“Selective Plugging of Formations with Foam”
US 3,994,344
November 30, 1976, Robert H. Friedman, Assignment: Getty Oil Corp.
“Method For Recovery of Acidic Crude Oils”
US 4,074,757
February 21, 1978, Betty J. Fleber et. al., Assignment: Standard Oil Co.
“Method Using Lignosulfonates for High-Temperature Plugging”
US 4,081,030
March 28, 1978, David R. Carpenter et. al., Assignment: Dow Chemical Co.
“Aqueous Based Slurry With Chelating Agent and Method of Forming A Consolidated
Gravel Pack”
US 4,091,868
May 30, 1978, Eugene C. Kozlowski et. al., Assignment: Diversified Chemical Corp.
“Method of Treating Oil Wells”
US 4,257,813
March 24, 1981, Dan D. Lawrence et al Assignment: ARCO
“Formation Treatment With Silicate Activated Lignosulfonate Gel”
US 4,275,789
June 30, 1981, Dan D. Lawrence & Betty J. Felber, Assignment: Standard Oil Co.
Silicate Activated Lignosulfonate Gel Treatments Of Conductive Zones
US 4,293,440
October 6, 1981, Eugene A. Elphinstone et al Assign: Halliburton
“Temperature Gelation Activated Aqueous Silicate Mixtures and Process of Forming
Impermeable Gels”
US 4,300,634
November 17, 1981, Richard L. Clampitt, Assignment: Phillips Petroleum Co.
“Foamable Compositions and Formations Treatment”
US 4,389,320
June 21, 1983, Richard L. Clampitt, Assignment: Phillips Petroleum Company
“Foamable Compositions and Formations Treatment”
US 4,428,429
January 31, 1984, Betty J. Fleber et. al., Assignment: Standard Oil Co.
“Method For Sweep Improvement Utilizing Gel-Forming Lignins”

US 4,461,644
July 24, 1984, Jerry D. Childs, et al. Assign: Halliburton
“Light Weight Composition and a A Method of Sealing A Subterranean Formation”

US 4,485,875
December 4, 1984, David O. Falk, Assignment: Marathon Oil Company
“Process For Selectively Plugging Permeable Zones in a Subterranean Formation”

US 4,613,631
September 23, 1986, Wilton F. Espenscheid, Assignment: Mobil Oil Corp.
“ Crosslinked Polymers For Enhanced Oil Recovery”

US 4,640,361
February, 3, 1987, William H. Smith et al., Assign: Halliburton
“Thermally Responsive Aqueous Silicate Mixtures and Use Thereof”

US 4,744,418
May 17, 1988, Robert D. Sydansk, Assignment: Marathon Oil Company
“Delayed Polyacrylamide Gelation Process For Oil Recovery Applications”

US 5,168,928
December 8, 1992, Dralen T. Terry et. al., Assign: Halliburton
“Preparation and Use of Gelable Silicate Solutions In Oil Field Applications “

US 5,320,171
June 14, 1994, Mary Laramay, Assign: Halliburton
“Method of Preventing Gas Coning and Fingering in a High Temperature Hydrocarbon Bearing Formation”

US 6,059,035
June 9, 2000, Jiten Chatterji et al, Assign: Halliburton
“Subterranean Zone Sealing Methods and Compositions”

US 6,059,036
May 9, 2000, Jiten Chatterji et al, Assign: Halliburton
“Methods and Compositions For Sealing Subterranean Zone”

SPE 5609,
1975, W. O. Ford, Jr. et. al. Injection Engineering Services
“Field Results of A Short Setting Time Polymer Placement Technique”

SPE 13567
April 9-11, 1985, J. Meister, Sun E & P Co.,
“Bulk Gel Strength Tester”

SPE 15906
February 4-6, 1987, N. A. Mumallah, Phillips Petroleum Co.
“Chromium (III) Propionate: A Crosslinking Agent for Water Soluble Polymers in Real Oilfield Waters”

SPE 16253
February 4-6, 1987, S. K. Nanda et. al. Oil & Natural Gas Commission
“Characterization of Polyacrylamine-Cr+6 Gels Used for Reducing Water/Oil Ratio”

SPE 16274
February 4-6, 1987, A. Zaitoun et. al., Instutiute of Francais du Petrole
“The Role of Adsorption in Polymer Propagation Through Reservoir Rocks”

SPE 16963
September 27-30, 1987, R. S. Buell, H. Kazemi, Chevron & Marathon.

- “Analyzing Injectivity of Polymer Solutions With the Hall Plot”
SPE 17288
March 10-11, 1988, B> G> Mody et al. Profile Control Services, Inc.
“Proper Application of Crosslinked Polymer Decreases Operating Costs”
SPE 20998
February 20-21, 1991, Eniricerche SpA
“Chemical and Structural Studies on Cr+3/Polyacrlamide Gels”
SPE 21000
February 20-21, 1991, N. Kohler et. al. Institute Of Francais du Petrole
“Polymer Treatment for Water Control in High-Temperature Production Wells”
SPE 21001
February 20-21, 1991, J. Kolnes et. al. Rogaland U. Centre
“The Effect of Temperature on the Gelation Time of Xanthan/Cr(III) Systems”
SPE 21547
February 7-8, 1991, R. L. Clampitt et. al. R. L. Clampitt & Assoc.
“Applying a Novel Steam-CO₂ Combination Process in Heavy Oil & Tar Sands”